

General approach for studying first-order phase transitions at low temperatures

C. E. Fiore^{1,*} and M. G. E. da Luz^{1,†}

¹*Departamento de Física, Universidade Federal do Paraná, 81531-980, Curitiba-PR, Brazil*

By combining different ideas, a general and efficient protocol to deal with discontinuous phase transitions at low temperatures is proposed. For small T 's, it is possible to derive a generic analytic expression for appropriate order parameters, whose coefficients are obtained from simple simulations. Once in such regimes simulations by standard algorithms are not reliable, an enhanced tempering method, the parallel tempering – accurate for small and intermediate system sizes with rather low computational cost – is used. Finally, from finite size analysis, one can obtain the thermodynamic limit. The procedure is illustrated for four distinct models, demonstrating its power, e.g., to locate coexistence lines and the phases density at the coexistence.

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First-order phase transitions (FOPT) are ubiquitous in nature [1], associated to a countless number of processes [2]. Moreover, they take place in different temperature scales, e.g., from 2800 K in the Earth core-mantle [3] to few and near zero Kelvin range (for many systems, in a rather similar way [4]), or even being responsible for unique effects, but across a very broad range of T 's [5]. In special, FOPT at low temperatures underpin important phenomena, like field-induced metal-insulator transitions, magnetoresistance, superfluidity, and Bose-Einstein condensation, among many others.

So, it is understandable and desirable the multitude of approaches (mainly numerically [6] given the difficulty to obtain general exact results [7]) developed to study FOPT. In certain instances, nevertheless, many of them can face procedural difficulties, not leading to precise results for the sought thermodynamical quantities, say, the exact location of coexistence lines.

As particularly powerful methods we can cite cluster algorithms [8], multicanonical [9] and Wang-Landau [10]. In cluster, non-local configuration exchanges often ensure the crossing of even high free-energy barriers. But a drawback is its specialization: each model requires a specific and efficient algorithm to implement the transitions, not available in many cases. On the other hand, Wang-Landau and multicanonical are general and have been applied successfully in a great diversity of problems. However, the former may demand very large computational time to calculate the density of states, specially considering that the number of states can increase very fast with the system size [11]. The latter relies on histogram reweighting techniques to obtain the appropriate averages, a difficult task for large systems (see, e.g., [12]).

Given so, here we present a protocol to study FOPT at low temperatures by means of direct and simple numerical simulations. Extending previous results [13], it considers around any transition a general parametric analytical expression for relevant thermodynamic quantities (like order parameter, density, magnetization, compressibility, etc). The parameters are then obtained by simulating small systems, making the approach compu-

tationally fast. Finally, from proper extrapolations, the correct thermodynamic limit is obtained. Once standard algorithms usually fail for FOPT at low T 's, even for small systems, we consider tempering methods (already shown reliable for FOPT, see [14, 15] and Refs. therein). Thus, we use the parallel tempering, PT, very efficient for small and intermediate system sizes. As we exemplify with four different lattices models, the approach leads to a precise way to determine the coexistence regions.

We begin recalling a rigorous analysis for finite systems having \mathcal{N} coexisting phases at ξ^* , with ξ an appropriate phase transition parameter control (e.g., temperature or chemical potential). It has been shown [16] that at low T 's and around ξ^* , the partition function is very accurately given by $Z = \sum_{n=1}^{\mathcal{N}} \alpha_n \exp[-\beta V f_n]$, with $\beta = (kT)^{-1}$. For the phase n , f_n is the (metastable) free energy [16] per volume V and α_n is the degeneracy, resulting from eventual symmetries of the problem.

Next observe that $W = -\partial_{\xi} \ln[Z]/(\beta V)$ ($\partial_x \equiv \partial/\partial x$) is frequently the start point to calculate distinct order parameters (density, magnetization, etc). Since close to ξ^* , $f_n \approx f^* + f_n'^* y$ [17] for $f_n'^* = \partial_{\xi^*} f_n(\xi^*)$ and $y \equiv \xi - \xi^*$, we find the following general form for W :

$$W = (b_1 + \sum_{n=2}^{\mathcal{N}} b_n \exp[-a_n y]) / (1 + \sum_{n=2}^{\mathcal{N}} c_n \exp[-a_n y]). \quad (1)$$

The coefficients a_n , b_n and c_n depend on ξ^* , $f_n'^*$, T , and other system parameters. But only the a_n 's are (linear) functions of V . Then, at the coexistence ($y = 0$) W is independent on the volume and for all V the curves $W \times \xi$ cross at $\xi = \xi^*$. In this way, Eq. (1) can be used not only to locate the transition point, but also to determine the coexistence order parameters at the thermodynamic limit. Moreover, if the f 's are ordered such that $f_1'^* = f_2'^* = \dots = f_m'^* < f_{m+1}'^* < \dots < f_k'^* = f_{k+1}'^* = \dots = f_N'^*$, for $V \rightarrow \infty$ and $y \rightarrow 0^{\pm}$ we have $W_{\pm} = \sum_{n=v_{\pm}}^{n=u_{\pm}} b_n/c_n$, with $v_+ = 1, u_+ = m, v_- = k, u_- = \mathcal{N}$. For $k = \mathcal{N}$ ($m = 1$) W_+ (W_-) is given in terms of the sole phase which is immediately to the right (left) of ξ^* .

Thus, considering relatively small V 's we can obtain

the parameters a 's b 's and c 's and hence, from the curves W , appropriate order parameters and response functions – e.g., through derivatives of the order parameter – at the transition point. For instance, if $\xi = \mu$ is the chemical potential, $\rho(\mu, T) = -W$ is the density and $\chi = \partial_\mu \rho|_T$ is the isothermal compressibility. Finally, from a simple scaling analysis [18], but using analytical smooth expressions, the thermodynamical properties are determined.

The above will work properly only with methods which correctly sample the configuration space [8, 10], yielding reliable fittings for Eq. (1) parameters. Often, this is not so when systems displaying strong discontinuous transitions are simulated by conventional one-flip approaches, even for small sizes. The solution is then to consider enhanced sampling, like parallel [19] and simulated [20] tempering algorithms, PT and ST. Since the former is particularly appropriate for FOPT (see [14] for details as well as for implementation), here we use the PT in our “combo” procedure for phase transitions at low T 's.

To illustrate the protocol, next we analyze four different lattice models displaying strong FOPT at low T 's. In each case, what operationally sets a low temperature is the validity of the previous Z decomposition. Physically, it corresponds to T 's for which there is no overlap between the peaks of the order parameter bimodal distribution at the coexistence. In all examples we perform accurate numerics with the PT algorithm and compare with the general Eq. (1), whose parameters are always obtained using only four points from the simulations.

As the first example, we consider a rather complex system, the associative lattice-gas (ALG) model [23], aimed to reproduce liquid polymorphism and water-like anomalies. A site i may or may not be occupied ($\sigma_i = 1$ or 0) by a molecule in a triangular lattice. The orientational variable $\tau_i^{ij} = 0, 1$ represents the possibility of hydrogen bonding (in a maximum of four) between the molecule in site i and those in the adjacent six neighbors j , provided $\tau_i^{ij} \tau_j^{ji} = 1$. Two first neighbor molecules have an interaction energy of $-v$ ($-v + 2u$) if there is (there is not) a hydrogen bond between them. The Hamiltonian reads

$$\mathcal{H} = 2u \sum_{\langle i,j \rangle} \sigma_i \sigma_j [(1 - v/(2u)) - \tau_i^{ij} \tau_j^{ji}] - \mu \sum_i \sigma_i. \quad (2)$$

It presents one gas and two liquid, LDL and HDL, phases of densities $\rho = 0$, $\rho = 3/4$, and $\rho = 1$, respectively. For fixed T , by increasing μ we pass through two FOPT, namely, gas-LDL and LDL-HDL.

We study the ALG model gas-LDL and LDL-HDL FOPT by plotting the density vs μ for $T = 0.300$, $u = v = 1$, and different V 's. For the gas-LDL case, we show the results in Fig. 1 (a). We clearly see a good coincident crossing of all curves at $\mu = -1.9986(2)$, for $\rho = 0.600(1)$. The exact transition density $\rho = 3/5 = 0.6$ is understood recalling that at the coexistence both gas ($\rho = 0$) and LDL ($\rho = 3/4$) phases have equal weight.

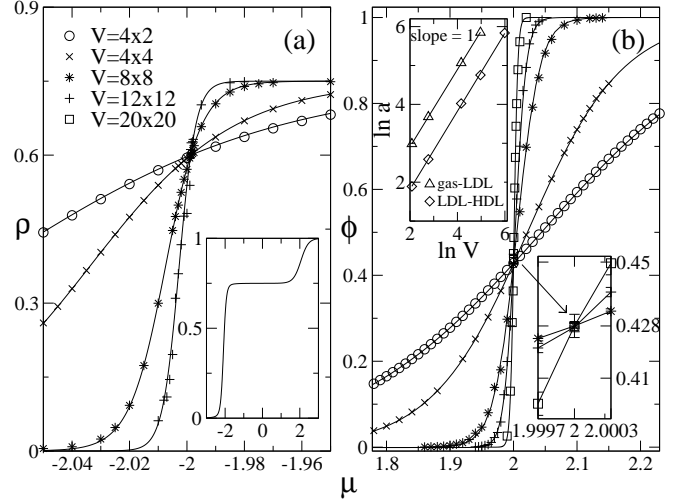


FIG. 1. The ALG model for the parameters as in the text and different $V = L \times L$. The continuous lines are curves from Eq. (1) for: (a) $\rho \times \mu$ around the gas-LDL transition (the inset shows $\rho \times \mu$ in the whole μ range where the two FOPS take place); and (b) $\phi (= 4\rho - 3) \times \mu$ around the LDL-HDL transition. The blow up shows the crossing for $L = 8, 12, 20$. The expected linear $a \times V$ behavior is displayed in the inset of (b) (the log-log scale is just for accommodating both cases). For comparison, the simulations for $V = 4 \times 2$ are exact.

Given that $\alpha_{LDL} = 4$, the value follows. Around LDL-HDL, ρ does not vanish, inset of Fig. 1 (a). Since $3/4$ (the totality) of the lattice is filled by molecules in the LDL (HDL) phase, a better order parameter is the rescaled density $\phi = (4\rho - 3)$. Thus, in Fig. 1 (b) we display $\phi \times \mu$ for the LDL-HDL transition. Again, all the isotherms are well described by Eq. (1), crossing at $\mu = 2.0000(3)$ with $\rho = 0.857(1)$. In Fig. 1 (b) inset we confirm the expected linear dependence on V for the parameter $a_2 = a$ (a single a once we have only two phases in each transition).

Next we consider the Bell-Lavis (BL) model, which also displays water-like anomalies. The sites may or may not be occupied ($\sigma_i = 1$ or 0) by molecules of two possible orientations. But differently from the ALG, the van-der-Waals interaction between two adjacent molecules is attractive, $-\epsilon_{vdw}$. So, there is no energetic punishment if hydrogen bonds (of energy $-\epsilon_{hb}$) are not formed. Such distinctions from the ALG, e.g., result in a second order phase transition for LDL-HDL, but still a FOPS for the gas-LDL. It is described by ($\zeta \equiv \epsilon_{vdw}/\epsilon_{hb}$)

$$\mathcal{H} = -\epsilon_{hb} \sum_{\langle i,j \rangle} \sigma_i \sigma_j [\tau_i^{ij} \tau_j^{ji} + \zeta] - \mu \sum_i \sigma_i. \quad (3)$$

For $\zeta < 1/3$, the BL presents three phases, gas ($\rho = 0$), LDL ($\rho = 2/3$ in a honeycomb structure), and HDL ($\rho = 1$) [21]. In the numerics we set $\epsilon_{hb} = 1$ and $\epsilon_{vdw} = 1/10$.

For $T = 0.25$, in Fig. 2 we plot $\rho \times \mu$ around the FOPT gas-LDL. Once more, the simulations are well described by Eq. (1). The isotherms cross at $\mu = -1.6528(1)$, with

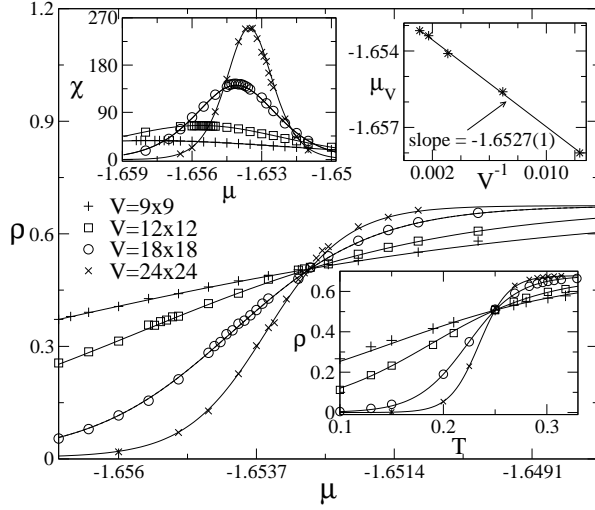


FIG. 2. For the BL model gas-LDL FOPT and parameters as in the text, $\rho \times \mu$ for distinct V 's and $T = 0.25$. All the continuous lines are properly obtained from Eq. (1). The upper insets show the isothermal compressibility χ vs μ and μ_V (the values of μ at the peaks of χ) vs V^{-1} . The lower inset shows $\rho \times T$ curves for $\mu = -1.6528$, which cross at $T = 0.25$.

$\rho \approx 0.507(2)$ very close to the exact $\rho = 1/2$ (which can be inferred as done for the ALG model). In the upper-left inset we show $\chi = (\frac{\partial \rho}{\partial \mu})_T$ by properly differentiating Eq. (1) (continuous lines) and by numerically simulating $\chi = V(\langle \rho^2 \rangle - \langle \rho \rangle^2)$. Note the remarkable agreement, again illustrating the power of Eq. (1) to describe relevant thermodynamic quantities around FOPT. The upper-right inset displays the values of $\mu = \mu_V$ (for which χ is maximum) vs V^{-1} . This type of scaling extrapolation also can give the thermodynamic limit for the transition, here $\mu = -1.6527$, basically the same value obtained from the crossing. Finally, instead of μ one could take T as the control parameter. Setting $\mu = -1.6528$ and varying T we see in the lower inset of Fig. 2 the gas-LDL transition. As it should be, the curves cross at $T = 0.25$, with $\rho \approx 1/2$. Finally, we note that for $T > 0.43$, the results from the present method starts to be less accurate.

The Blume-Emery-Griffiths (BEG) model yields [24]

$$\mathcal{H} = - \sum_{\langle i,j \rangle} [J\sigma_i\sigma_j + K\sigma_i^2\sigma_j^2] - \sum_i [H\sigma_i - D\sigma_i^2], \quad (4)$$

where a site i is either empty or occupied by two different type of species ($\sigma_i = 0, \pm 1$). Parameters J and K are interaction energies and D and H denote linear combination of the species μ 's. This system is a particularly interesting test because the otherwise very reliable cluster algorithm for the BEG model [8] fails for some particular K/J 's, e.g., the value we address $K/J = -0.5$. So, for a better comparison with our procedure, we also propose a new cluster-Metropolis hybrid approach, which includes intermediary Metropolis algorithm steps (details will appear elsewhere). We note, nevertheless, that the

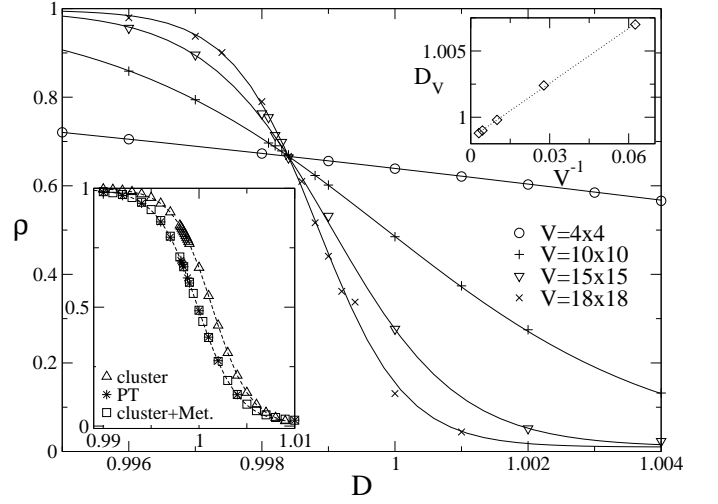


FIG. 3. For the BEG model, $\rho \times \mu$ for parameters as in the text and distinct V 's. The results for $V = 4 \times 4$ are exact. The continuous lines properly come from Eq. (1). The right inset shows D_V (D for which χ is maximum) vs V^{-1} . The left inset compares numerical simulations from the PT, cluster and hybrid cluster-Metropolis algorithms for $V = 10 \times 10$.

Metropolis alone is not able to cross the high free energy barriers at the phases coexistence.

In Fig. 3 we plot $\rho \times D$ for $H = 0$, $J = 1$, $K = -0.5$, $T = 0.20$, and different V 's. We have a FOPT with all the isotherms crossing at $D = 0.9984(1)$ and $\rho \approx 2/3$. The right inset of Fig. 3 shows the position D_V of the peak of $\chi = -(\frac{\partial \rho}{\partial D})_T$, calculated directly from Eq. (1). A linear extrapolation of $D_V \times V^{-1}$ gives $D = 0.99845(5)$, in excellent agreement with the crossing value. For $V = 10 \times 10$, we plot in the left inset simulations from the usual cluster, the improved (but dedicated) cluster-Metropolis, and PT algorithms. The latter two display very good concordance, with the cluster given poorer results. We should mention that for the BEG and ALG models there are no precise simulations in the literature for the parameter conditions here considered.

Lastly, we discuss the asymmetric Ising Hamiltonian on a triangular lattice (of sublattices (α, β, γ)) [25]

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i\sigma_j - K \sum_{\langle i,j,k \rangle} \sigma_i\sigma_j\sigma_k - H \sum_i \sigma_i. \quad (5)$$

The second sum is over first neighbors trios forming triangles. Using the Wang-Landau method [10], the model has been studied in details [26] (but for larger systems and lower numerical precision). It displays one ferromagnetic, $(- - +)$, and two ferromagnetic, $(+ + +)$ and $(- - -)$, phases. For very low temperatures, by increasing H the system displays a second-order phase transition $(- - -) \rightarrow (- - +)$ and then a FOPT $(- - +) \rightarrow (+ + +)$. The $(- - +)$ phase disappears in a critical endpoint ($T_c = 2.443(1)$, $H_c = -2.934(1)$), above it giving rise only to a FOPT between the two ferromagnetic phases.

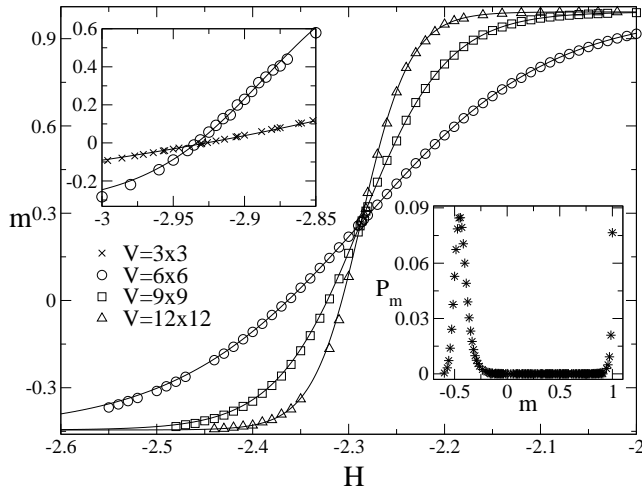


FIG. 4. For the asymmetric Ising model and parameters as in the text, $m \times H$ for distinct V 's and $T = 5.00$ ($T = 2.40$, left inset). Continuous lines are the curves from Eq. (1). The right inset shows $P_m \times m$ for the $T = 5.00$ case.

Although the magnetization per site m is not the actual order parameter, for rather small system sizes we can extract from it any relevant FOPT information.

In Fig. 4 we plot $m \times H$ for $J = 1, K = 2$ and $T = 5.00$ for the $(---) \rightarrow (+++)$ FOPT. We see that Eq. (1) represents quite well the transition. In the right inset we show the histogram magnetization density probability P_m vs m for $L = 12, T = 5.00$ and $H = -2.3325$, illustrating further that the phases coexistence is being properly characterized [14]. Likewise, the FOPT $(---) \rightarrow (+++)$ for $T = 2.40$ in the left inset is well described by our method. All the isotherms cross at $H = -2.2863(5)$ and $H = -2.9357(5)$ (left inset), in fair agreement (given the different numerical accuracies) with the estimates $H = -2.284(1)$ and $H = -2.939(1)$ by the authors of Ref. [26] (private communication).

By considering Eq. (1), derived from rigorous results at low T 's, we have proposed a general protocol to study FOPT. It is accurate and demands only few simulations for relatively small systems, hence a computationally low cost procedure. The approach has been very successfully applied to four distinct lattice models. Of course, more analyzes, e.g., for higher dimensions and continuous systems (presently under progress, but with promising preliminary findings) are in order as further tests. Nevertheless, we believe the method already shows itself a valuable tool to analyze the very important problem of FOPT at low temperatures.

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* fiore@fisica.ufpr.br

† luz@fisica.ufpr.br

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